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Laboratory Evaluation of NOx Reduction Techniques for Refinery CO Boilers

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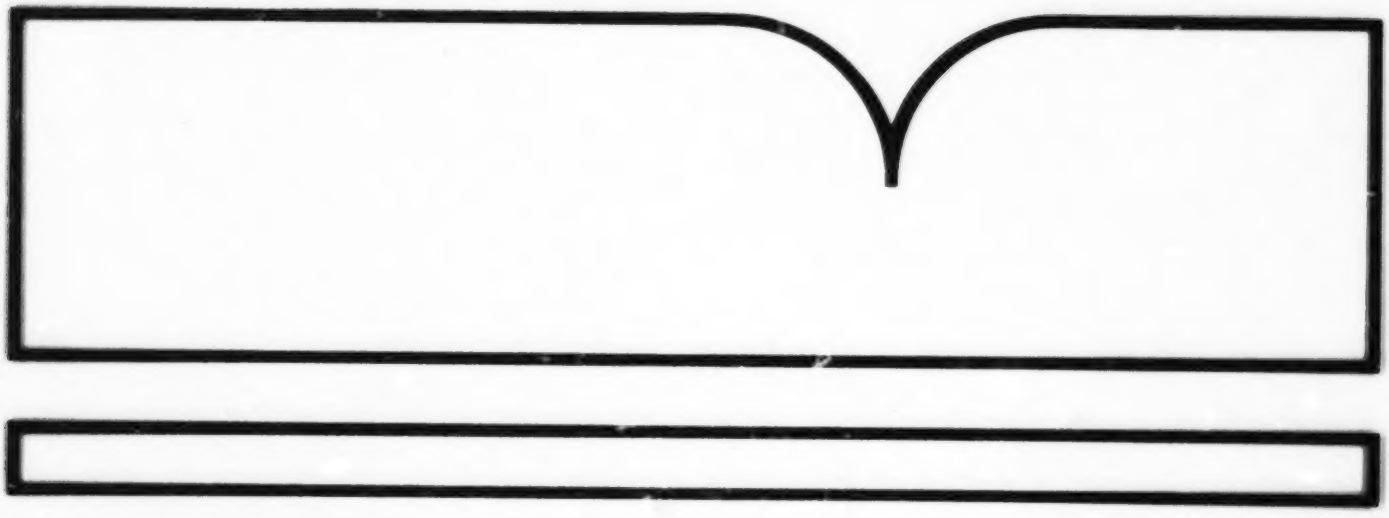

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LABORATORY EVALUATION OF NO_x REDUCTION TECHNIQUES FOR REFINERY CO BOILERS

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16. ABSTRACT The paper gives results of work to develop and demonstrate, in the laboratory, NOx reduction techniques that would be suited to petroleum refinery CO boilers. (NOTE: Most refineries have one or more CO boilers to incinerate off-gases from catalytic cracking. These devices constitute a significant fraction of total refinery NOx emissions. Methods used to reduce NOx emissions from conventional boilers either are not applicable or have performed poorly when applied to refinery CO boilers.) The program had three major objectives: (1) to simulate in the laboratory a full-scale refinery CO boiler, (2) to investigate the effects of operational variables on NOx formation in the boiler furnace, and (3) to evaluate combustion modification techniques to reduce the NOx emissions. All program objectives were achieved on a natural-gas-fired, single-burner, horizontal furnace with CO gas admitted via a concentric annulus around the burner throat (the ratio of CO-gas to total stack gas was about 0.65, dry, and the CO-gas contained about 2% CO, 500 ppm NH3, and 120 ppm NOx). The most important variables influencing NOx level are the NH3 content of the CO-gas and burner stoichiometry (air/fuel ratio). Air staging was found to be the best NOx control method (adding staged air well downstream of the burner with good cross-mixing produced the best results).

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Refineries	Combustion Control	Stationary Sources	13I	21B
Nitrogen Oxides	Ammonia	Air Staging	07B	
Catalytic Cracking	Stoichiometry		13H, 07A	07D
Carbon Monoxide	Natural Gas			21D
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Introduction

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Most petroleum refineries contain one or more carbon monoxide (CO) boilers for the incineration of off-gases from catalytic cracking operations. These devices constitute a significant fraction of total refinery nitrogen oxide (NO_x) emissions. Methods that have been used to reduce NO_x emissions from conventional boilers either are not applicable or have performed poorly when applied to refinery CO boilers. The purpose of the work reported here was to develop and demonstrate, in the laboratory, NO_x reduction techniques that would be specifically suited to refinery CO boilers.

Program Objectives and Description

The program had the following three major objectives: (1) to simulate in the laboratory a full-scale refinery CO boiler, (2) to investigate the effects of operational variables on NO_x formation in the boiler furnace, and (3) to evaluate combustion modification techniques to reduce the NO_x emissions.

A model CO boiler was constructed in KVB's combustion laboratory. This model, which operated in the range of 0.3 to 0.6 MW total heat input, was based on a full-scale CO boiler that had been tested extensively by KVB. The full-scale boiler selected employed a single multi-injector burner and a horizontal furnace cavity. The burner, CO-gas entry throat, and furnace were scaled down from the full-scale boiler based on preservation of critical velocities, residence times, and heat transfer parameters.

General Description of a Refinery CO Boiler

The primary function of a refinery CO boiler is to incinerate the CO-containing off-gas from the catalytic cracking operation. Virtually all gasoline-producing refineries now use the fluidized catalytic cracking (FCC) process to upgrade the paraffinic contents of gasoline feedstocks. The catalyst employed in this process is subject to "coking;" i.e., accumulation of carbonaceous residue on the surfaces of catalyst particles. To remove the coke layer and thus reactivate the surface, the catalyst is circulated through a fluidized combustion unit known as a regenerator. In this unit, the coke layer is burned off the catalyst particles at approximately 975 K. In order to limit temperature, slightly sub-stoichiometric quantities of air are admitted to this process, resulting in a regenerator off-gas containing typically a few percent CO. The regenerator off-gas, commonly referred to as CO-gas, is incinerated in the CO boiler. The typical FCC unit/CO boiler arrangement is shown schematically in Figure 1. In most cases, depending upon whether the regenerator includes heat recovery devices, the CO-gas also represents a

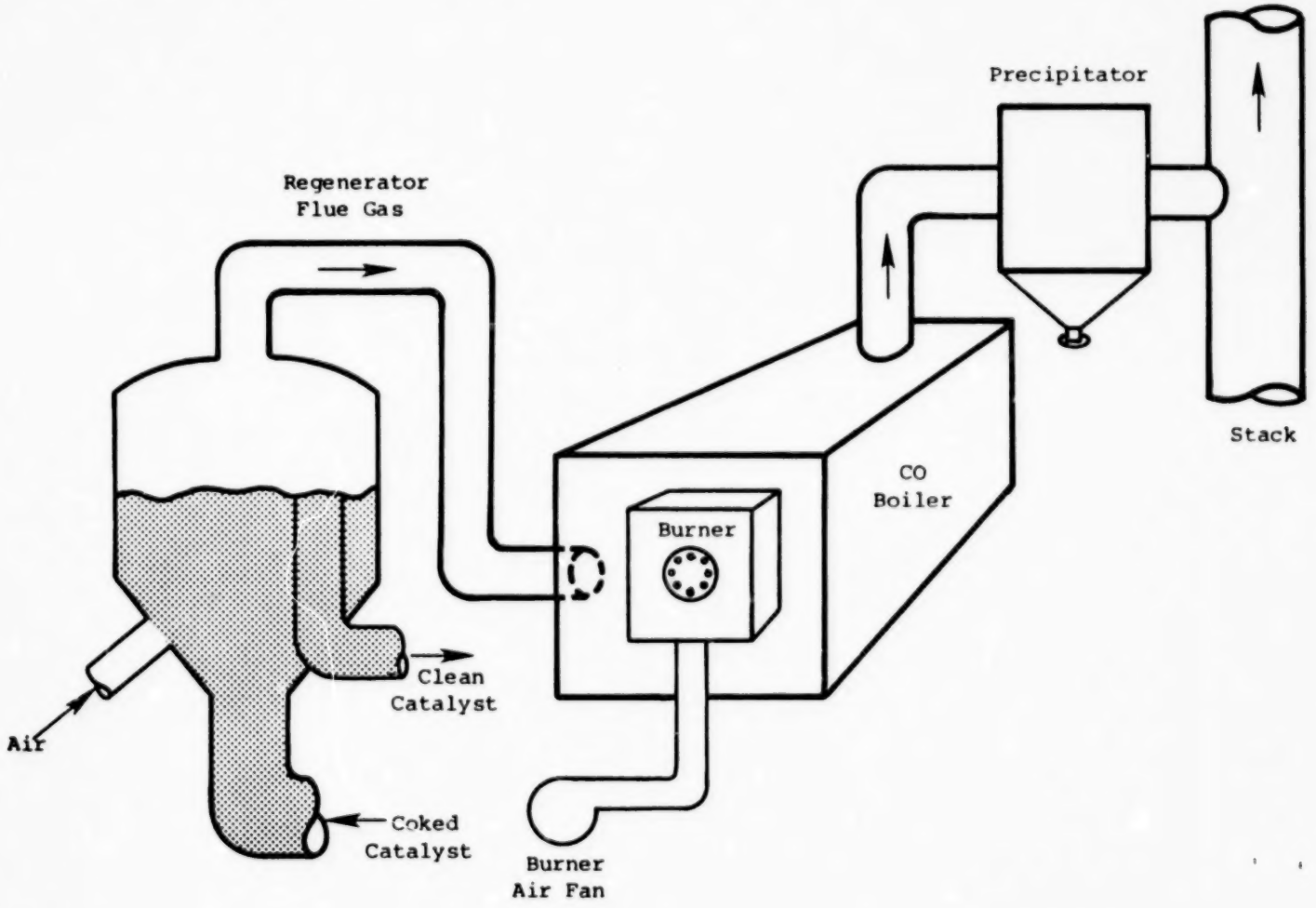

Figure 1. Schematic Drawing of Typical FCC Regenerator with CO Boiler

substantial amount of waste heat (typical flue gas temperatures in the 925-975 K range), the recovery of which is a secondary function of the CO boiler.

The coke deposit on the catalyst particles entering the FCC regenerator invariably contains nitrogen compounds. The presence of this organic nitrogen in an air-deficient combustion atmosphere leads to formation of ammonia (NH_3) and NO_x. Levels of NH_3 in the 400 to 1000 ppm range have been observed in the few cases in which measurements have been made. NO_x levels measured on one unit were much lower than this, in the 25 to 100 ppm range. The NH_3 and NO_x levels in the CO-gas are undoubtedly influenced by the amounts and types of nitrogen compounds in the refinery feedstock and are possibly influenced further by the regenerator operating conditions (temperature and stoichiometry). Recently, an alternate catalyst has been used in FCC units. This catalyst can be regenerated at a higher temperature without adversely affecting its reactivity. In this case, the catalyst is regenerated in an oxidizing atmosphere (excess oxygen) resulting in the production of higher concentrations of NO_x and lower concentrations of NH_3.

In the CO boiler, the CO-gas is incinerated by mixing with a high-excess-air flame from a conventional burner operated typically on refinery gas fuel. The fuel gas burner supplies both heat and oxygen for oxidation of virtually all of the CO to carbon dioxide (CO_2), if the unit is properly designed for rapid and complete mixing of the burner products with the CO-gas. This mixing must occur early in the furnace well before the gases contact convective cooling surface. In most cases, the unit must be designed for effective mixing over a range of fuel/CO-gas input ratios since the boiler may follow refinery steam demand by variation in fuel input rate while CO-gas flow rate remains essentially constant.

NO_x Formation and Destruction Mechanisms

Two significant NO_x formation mechanisms occur in the CO boiler furnace. The first and most important is oxidation of NH_3 entering in the CO gas (Reaction 1).

$$NH_3 + O_2 \rightarrow NO + H_2O \qquad (1)^*$$

This oxidation occurs in the presence of excess oxygen at temperatures above approximately 1300 K. The second significant mechanism is oxidation of molecular nitrogen entering in air (Reaction 2).

$$N_2 + O_2 \rightarrow NO \qquad (2)$$

This oxidation occurs at significant rates in the presence of excess oxygen at temperatures above approximately 1800 K.

---

*Reactions 1-5 represent complex reaction chains, showing only major species; therefore, they are not stoichiometrically balanced.

Three competing mechanisms that either destroy NO_x or reduce its formation also can occur in the CO boiler furnace. First, NH_3 can alternately be reduced to nitrogen through its reaction with NO at temperatures ranging between approximately 1370 and 1480 K. The reaction will proceed only under fuel-rich conditions (Reaction 3).

$$NH_3 + NO \xrightarrow{\text{fuel}} N_2 + H_2O \qquad (3)$$

Second, NO_x already formed can be reduced to nitrogen through its reaction with hydrocarbon species generally present in abundance under fuel-rich conditions (Reaction 4).

$$NO + (HC) \rightarrow N_2 + H_2O + CO_2 \qquad (4)$$

Third, NH_3 and NO_x can react in the presence of excess oxygen to form nitrogen within the 1200 to 1300 K (approx.) temperature range (Reaction 5).

$$NO + NH_3 \xrightarrow{O_2} N_2 + H_2O \qquad (5)$$

NO_x Reduction Approaches

Control of NO_x formation in conventional gas-fired boilers focuses mainly on suppression of Reaction 2, via adjustments to reduce simultaneous occurrence of high O_2 and high temperature levels. Common approaches are reduction of burner turbulence, staged air admission, and flue gas recirculation. The low-turbulence burner and gas recirculation approaches are inappropriate for CO boiler furnaces in view of the small fraction of total NO_x emanating from Reaction 2 and the need for rapid mixing in order to adequately oxidize the large quantities of CO.

NO_x control in the CO boiler furnace should focus on Reaction 1, the main source of NO_x. Suppression of Reaction 1 appears more likely to result in a reliable NO_x control as opposed to working with the sensitive kinetics of Reaction 5. Methods to suppress Reaction 1 will also generally suppress Reaction 2 and enhance Reactions 3 and 4, and thus result in the greatest reduction in NO_x emissions. Possible design approaches to reduce NO_x formation via Reaction 1 are listed in Table I. These are all variations of combustion staging; i.e., staged admission of air and/or fuel in order to reduce available oxygen in the initial burning zone or create a fuel-rich preburning zone.

Under air staging, as indicated in Table I, five methods can be considered. The first, use of staged air ports located around the burner, has the advantage of requiring very little furnace modification but may not sufficiently reduce O_2 levels in the front of the furnace. The second, an air lance on the burner centerline, requires more hardware but creates a more distinct staging effect and can direct second stage air where needed to burn

Table I. NO_x reduction approaches for refinery CO boilers.

Air Staging
• Air ports around burner
• Air lance on burner centerline
• Air ports on furnace sidewalls
• Air register bias
• Selected fuel injectors out-of-service
Fuel Staging
• Fuel lances around burner
• Low-velocity fuel injection
• Fuel injectors aimed away from burner centerline
• Fuel diverted to CO-gas
• Fuel/air injectors on furnace sidewalls

out CO in the back portion of the furnace. The third, staged air ports located on the furnace walls, requires significantly more modification work than center air. However, it may have the best chance of burning out CO in the back portion of the furnace if center air proves inadequate. The last two methods, air register bias and taking selected fuel injectors out of service (terminating fuel flows), are by far the easiest to deploy. However, they probably create the least distinct staging effect and may be operationally difficult.

A second approach to promoting Reactions 3 and 4 is to direct a portion of the fuel supply outward from the burner centerline in an effort to generate a more fuel-rich atmosphere in the CO-gas prior to its mixing with excess air from the burner. As indicated in Table I, five methods of creating this fuel-rich outer zone can be considered. One is to divert part of the fuel to a set of injectors located around the burner. The second two are to aim the gas injectors away from the burner centerline or to redesign the injectors for lower injection velocity in order to reduce penetration of fuel toward the burner centerline. The success of the fuel diversion approach depends on the relative rates of the heat transfer, mixing, and kinetic processes involved. To the degree that adequate temperature can be generated in the CO-gas prior to its mixing with excess air and that the kinetics of Reactions 3 and 4 are sufficiently rapid, this approach will be effective in reducing NO_x. As indicated in Table I, this method can be extended from diverting fuel outward to adding a portion of the fuel directly to the CO-gas upstream of the furnace. Use of fuel and air injection downstream in the furnace can also be considered. This approach, in which the burner products are processed through a fuel-rich zone followed by a final burnoff zone, has been shown to be effective on utility boilers.

Experimental Methods

The sub-scale CO boiler design was based on a full-scale unit which KVB had tested in the field. This unit has a single-burner horizontal furnace with a superheater, side tube passes, and a topside economizer.

The sub-scale unit employed an existing water-cooled test furnace rated at 0.88 MW_t to which a scaled-down version of the full-scale boiler front end was retrofitted. The furnace front included a multi-injector gas burner with a concentric CO-gas entry throat (Figure 2) scaled down from the full-scale unit. CO-gas was introducted tangentially to the furnace in a manner similar to the method used in the full-scale unit. Scaling was based on critical entry velocities and furnace residence times. The furnace contained a torus (donut) shaped air plenum which can be located at a variable distance from the burner for supply of second stage combustion air simulating furnace wall NO_x ports (Figure 3). The firing face was equipped with eight NO_x ports arranged around the burner (see Figure 2) and supplied directly from the windbox. The burner could accommodate an air lance for center air staging. The burner gas injectors were adjustable in terms of both immersion depth and orientation of gas orifices. Selected injectors could be relocated to the NO_x ports to achieve the fuel-staging effect discussed above.

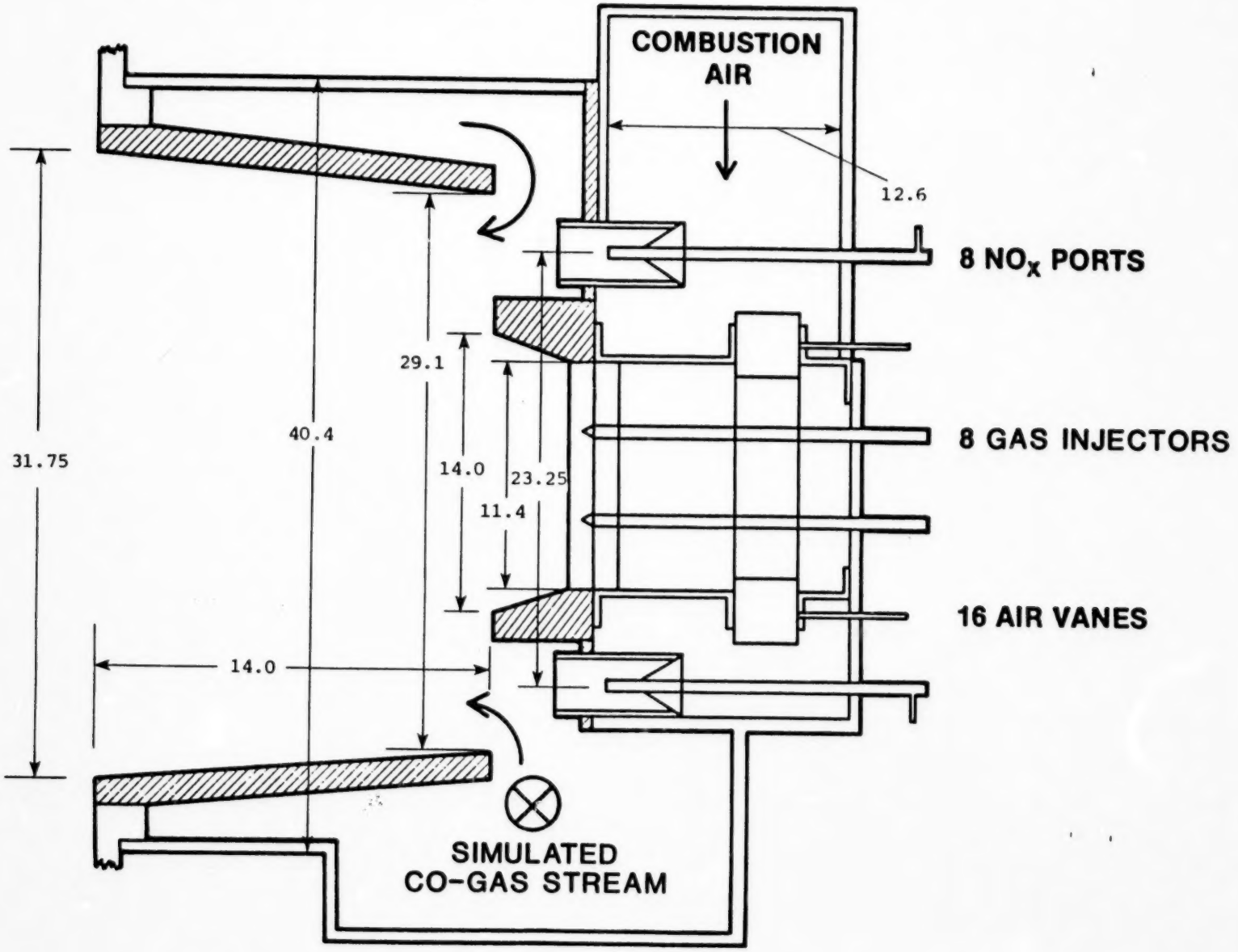

Figure 2. Schematic of Burner and CO-Gas Entry Throat (dimensions in centimeters)

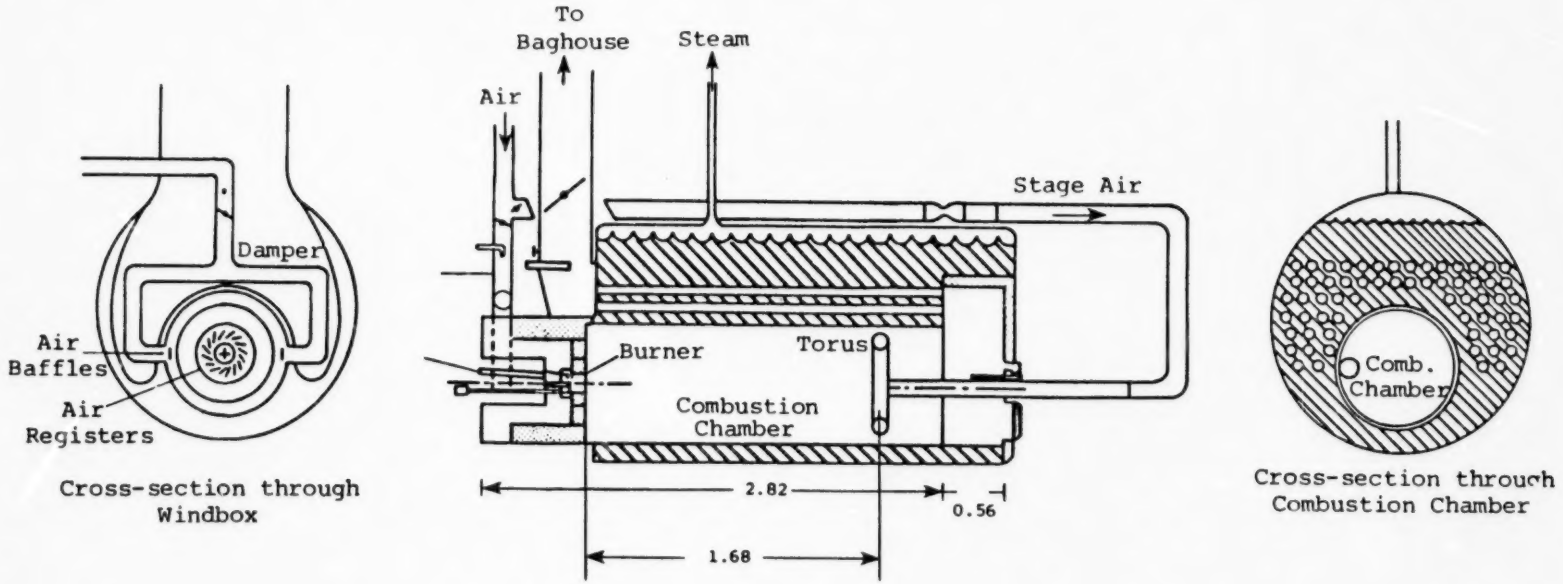

Figure 3. Schematic of the Test Boiler
(dimensions in meters)

The CO-gas supplied to the simulated CO boiler was generated in a second test furnace by operating that furnace fuel-rich. A schematic of the overall system is shown in Figure 4. Control of CO content of the CO-gas was effected by variation of combustion stoichiometry. Control of gas temperature was effected by blending hot gas removed directly from the furnace with cooler gas that had passed through the boiler firetubes. NH_3 and NO_x levels in this gas were controlled by adding NH_3 (1) to the fuel burned in the CO-gas generator to produce NO_x and, (2) to the CO-gas to simulate the desired NH_3 level.

Results

Table II compares the laboratory model with the full-scale boiler in terms of key operating parameters as well as NO_x and CO levels produced. This comparison shows the laboratory model to comprise a good working facsimile of the full-scale boiler. The ranges of data shown for the full-scale boiler were based on engineering and source tests conducted by local and state air quality control agencies and KVB during 1980-1982.

The following paragraphs will first discuss the effects of operating variables on NO_x and will then discuss the effectiveness of the various NO_x control techniques that were tested.

The NO_x parameter of primary interest was the net NO_x formed in the CO boiler furnace; i.e., after subtracting NO_x entering with the CO gas:

$$NO_x^N = NO_x^S - NO_x^R \cdot R \qquad (6)$$

where

NO_x^N = net NO_x formed in CO boiler furnace, ppm (dry)

NO_x^S = NO_x measurement in stack, ppm (dry)

NO_x^R = NO_x measurement in CO-gas, ppm (dry)

R = volumetric ratio of CO-gas to total stack gas (dry)

In addition, the stack NO_x data were corrected for minor variations in NO_x and NH_3 levels in the CO gas.

Except where intentionally varied, all operational variables were held within the following ranges:

CO-Gas Composition	
CO	2.1-2.5%
NH_3	490-515 ppm
NO_x	110-120 ppm
Ratio of CO-gas to stack gas	~0.65
CO boiler burner stoichiometry	~2.25

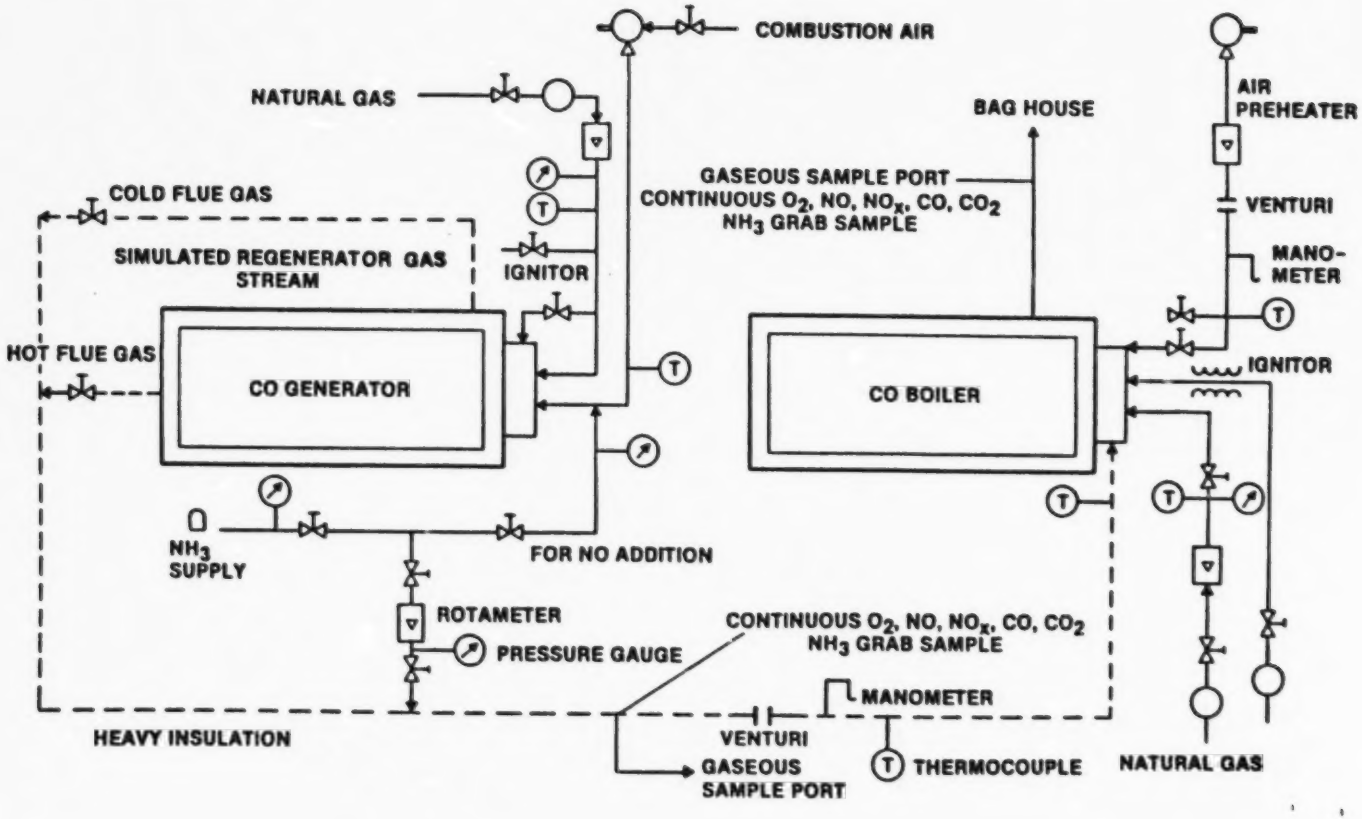

Figure 4. Schematic of Laboratory CO Boiler Simulation System

Table II. Comparison of operating ranges and NO_x levels produced -- laboratory boiler versus full-scale boiler.

	Normal Operation With CO-Gas		Boiler Only - No CO-Gas	
	Full-Scale	Laboratory	Full-Scale	Laboratory
CO-Gas (dry):				
CO, %	1.8-3.4	1.2-4.8	--	--
NO_x, ppm	45-120	48-150	--	--
NH_3, ppm	470-620	490-675	--	--
Temp., K	~975	~935	--	--
Fuel to Burner, MW_t	~20.5	~0.2		
Stack Gas (dry):				
O_2, %	1.0-3.5	1.4-3.6	3.4-3.6	3.5
CO, ppm	50-700	30-265	120-600	30-40
NO_x, ppm[a]	105-270	117-325	40-51	40-60
Dry Volumetric Ratio of CO-gas to stack gas	0.52-0.62	0.54-0.71	--	--

[a]Corrected to 3% O_2

Effects of Operating Variables

The most significant operating variables affecting NO_x formation in the CO boiler furnace are the NH_3 content of the CO-gas (NH_3^R) and the stoichiometry (fraction of stoichiometric air) at which the burner operates. Figure 5 shows the effects of these two variables with other operating variables held virtually constant. The data were correlated to both burner and furnace stoichiometry (S1 and S2, respectively), defined as:

$$S1 = \frac{\text{air to burner}}{\text{air required to burn fuel entering via burner}}$$

$$S2 = \frac{\text{air to burner}}{\text{air required to burn all fuel, CO, and } H_2 \text{ entering furnace}}$$

The data correlate best with burner stoichiometry (S1), and do not correlate as well with furnace stoichiometry (S2). The NO_x emissions did not correlate with furnace stoichiometry since the combustion air and CO-gas did not mix instantly. The CO-gas was introduced around the burner, while all combustion air entered through the burner. Having more or less fuel ($CO + H_2$) in the CO-gas did not therefore directly influence the overall combustion stoichiometry in the flame basket. Burner stoichiometry, on the other hand, dictated the level of oxygen available to react with CO-gas producing NO_x by the oxidation of the NH_3. Higher burner stoichiometry provided larger quantities of oxygen to more efficiently convert the NH_3 to NO_x. Conversely, lower burner stoichiometry minimized the amount of oxygen available and thus inhibited the NH_3 conversion to NO_x.

Figure 6 shows the aggregate and marginal conversion rates of NH_3^R to NO_x versus burner stoichiometry at approximately 500 ppm NH_3^R. Aggregate conversion rate is the fraction of total NH_3^R appearing as NO_x in the stack. Marginal conversion rate is the fraction of a small increase in NH_3^R that appears as an increase in NO_x in the stack. The data plotted in this fashion clearly show the strong effect of burner stoichiometry on NH_3 conversion rate, which varies from 10 to 55 percent depending on the stoichiometry. This plot also shows that the conversion rate approached zero at a burner stoichiometry of approximately 1.5 or less.

Figure 7 shows the effect of NO_x concentration in the CO-gas on NO_x in the stack; i.e., the NO_x survival rate as it passes through the furnace. Under typical unstaged combustion conditions, approximately 75 percent of the NO_x in the CO-gas appears in the stack (slope of the curve in the figure divided by R, the dry volumetric ratio of CO-gas to stack gas). When combustion is staged, in this case by stopping fuel flow to selected injectors, the survival rate of regenerator NO_x is decreased, as expected. Also as expected, the data indicate that the survival rate has a strong dependence on burner stoichiometry.

Figure 8 summarizes the effect of burner stoichiometry on NO_x formation in the furnace under two conditions: with 500 ppm NH_3 in the CO-gas (upper curve) and with no NH_3 in the CO-gas (lower curve). The upper curve

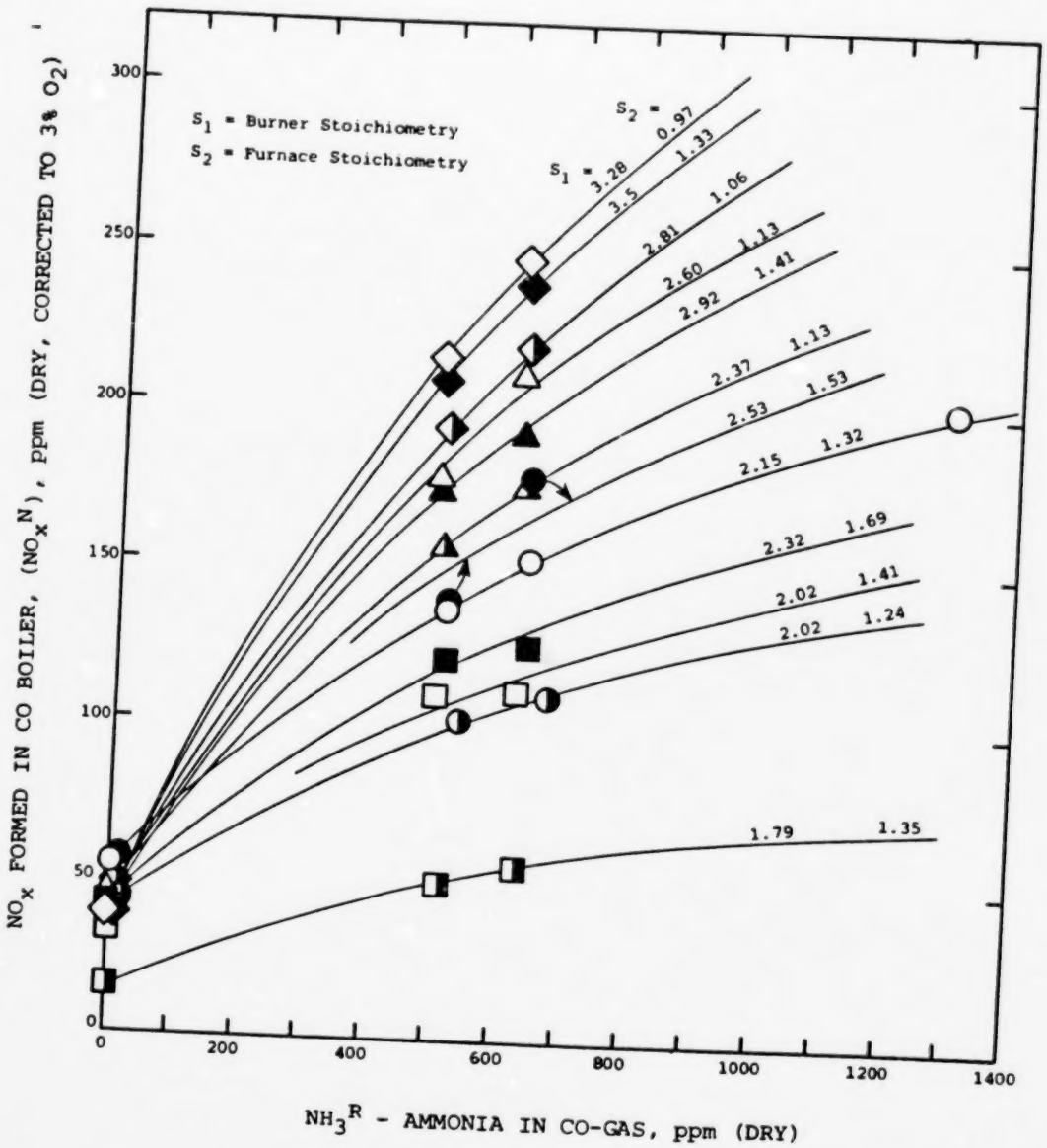

Figure 5. Effect of Ammonia Content of CO-gas and Burner Stoichiometry on NO_x Formation in CO Boiler

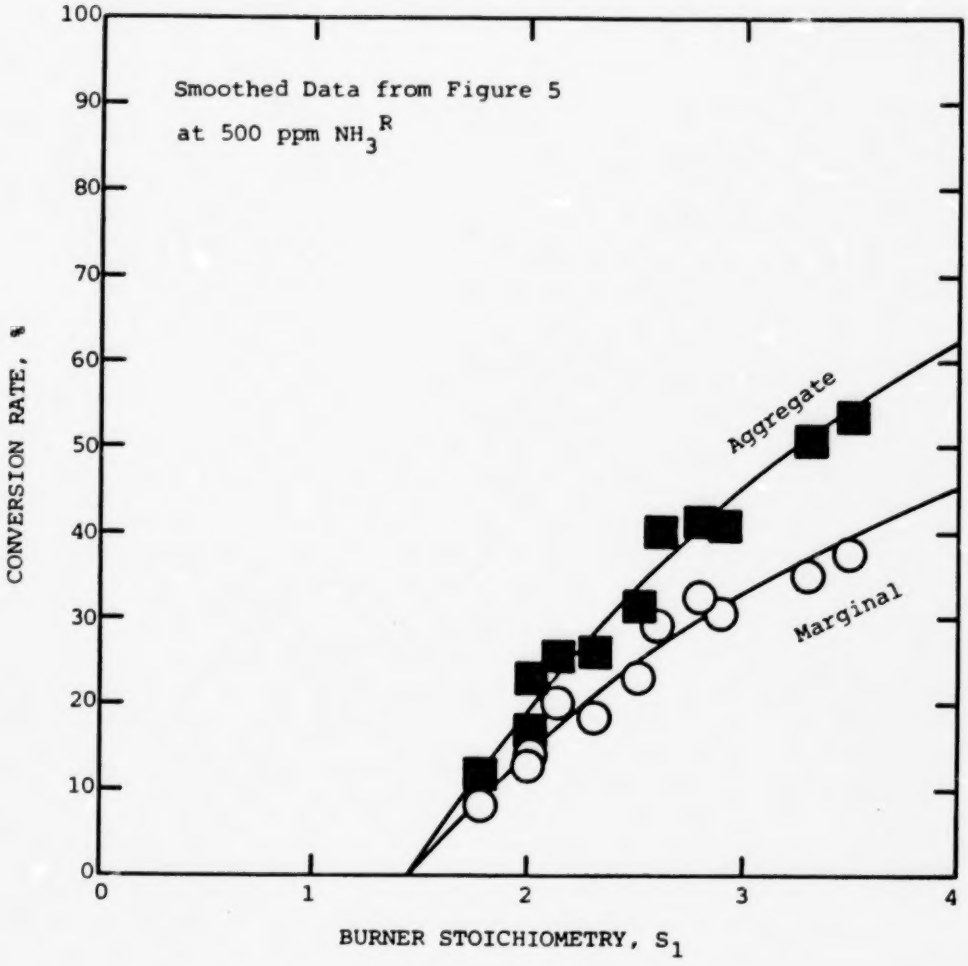

Figure 6. Effect of Burner Stoichiometry on Conversion of Ammonia to NO_x

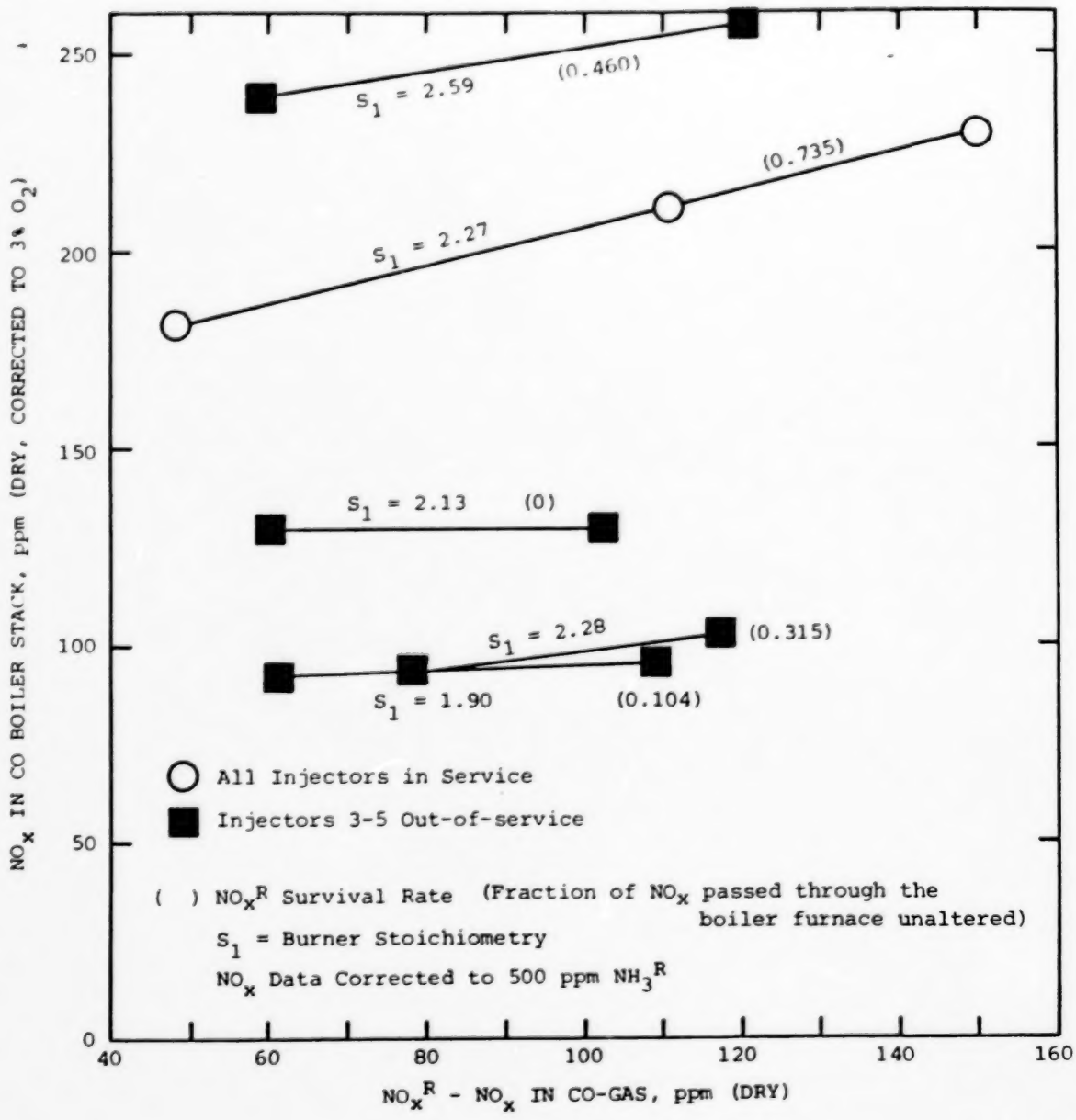

Figure 7. Effect of NO_x in CO-gas on NO_x in Stack

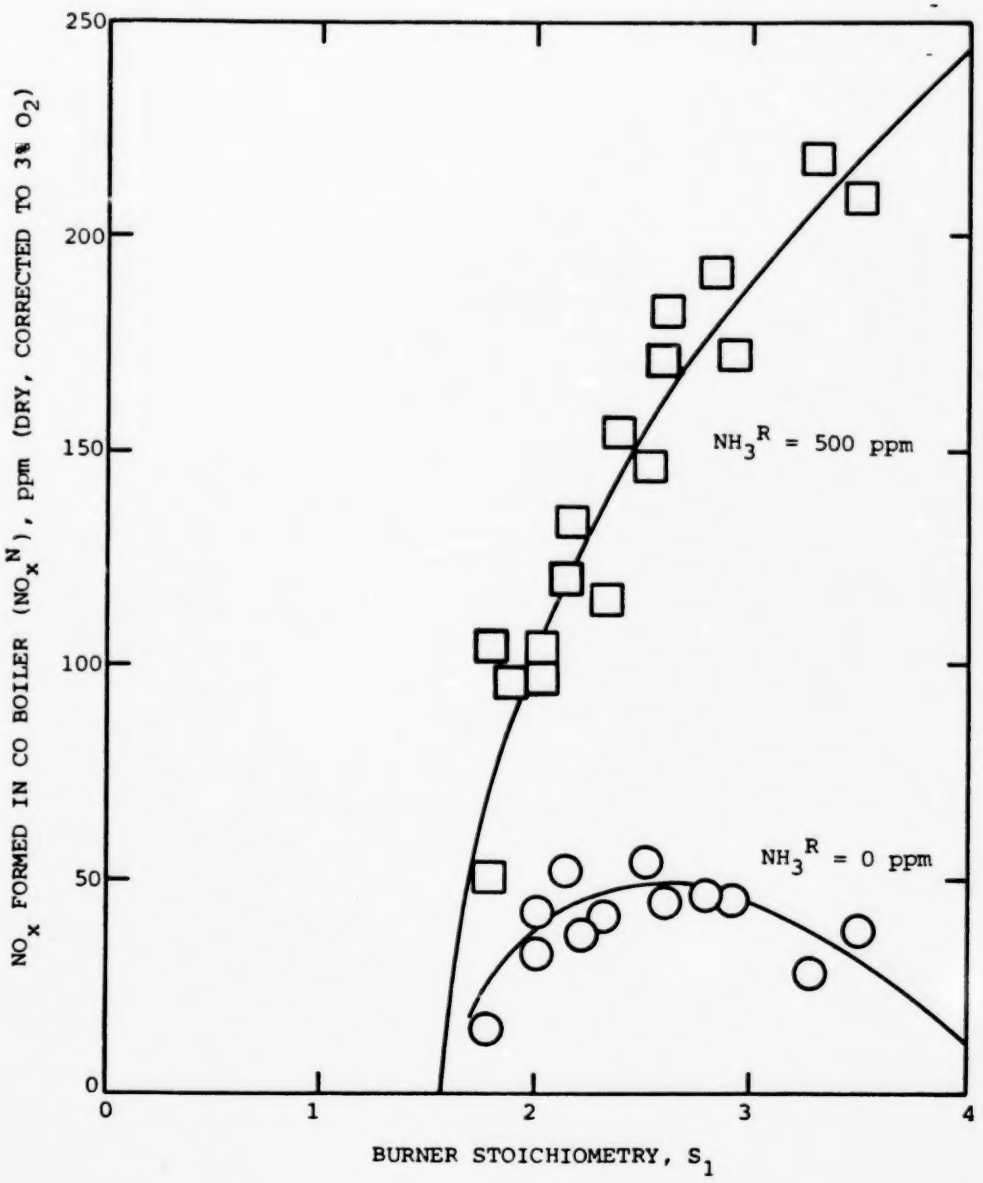

Figure 8. Effect of Burner Stoichiometry on NO_x Formation in CO Boiler

once again illustrates the strong effect of burner stoichiometry on NH_3 conversion to NO_x in the furnace. The lower curve indicates that thermal NO_x formation is enhanced by the introduction of the CO-gas. Tests with no CO-gas input indicated that the burner fundamentally produces a NO_x level in the range of 13 to 20 ppm (after dilution by CO-gas, corrected to 3 percent O_2). The fact that thermal NO_x levels much higher than this were produced when CO-gas was introduced indicates that the CO-gas plays some role in thermal NO_x formation either by raising the temperature of the burner flame zone or by producing sufficiently high temperatures in CO and H_2 combustion for NO_x formation to occur. In viewing the lower curve, it is also noted that net thermal NO_x formation declines as burner stoichiometry is either increased or decreased from approximately 2.6. The decline in thermal NO_x^N with decreasing stoichiometry probably reflects the reduced survival of regenerator NO_x at lower stoichiometries that was noted above in Figure 7; i.e., not an actual reduction in thermal NO_x which would not be expected at these still relatively high levels of burner air/fuel ratio. Reduction in thermal NO_x^N with increasing stoichiometry probably represents an actual decline in thermal NO_x resulting from cooling of the flame zone at excessively high levels of excess air.

An attempt was made to correlate the offset of individual data points from the upper curve in Figure 8 with furnace stoichiometry S2, stack O_2 level, and CO level in the CO-gas. None of these variables successfully correlated the offsets; thus, no secondary parameters were defined. It was noted that the stack O_2 level did not correlate well with overall air and fuel flows to the system. This may indicate that a problem was occurring with the stack O_2 measurement system.

Effectiveness of NO_x Reduction Techniques

All staging techniques basically achieve an extension of the NO_x-versus-stoichiometry effect shown in Figures 5 and 8. Design for second-stage burning of CO, however, enables operation at lower stoichiometries in the primary burning zone. Also, staging provides an added dimension of control in that burner stoichiometry can be controlled independently of overall furnace stoichiometry. The ability of various staging techniques to reduce NO_x without simultaneously increasing the CO level will be a key factor determining their usefulness. The CO characteristic of the unstaged burner is shown in Figure 9.

Referring to Table I, the methods involving air staging will be discussed first; i.e., fuel injectors out of service, air ports around the burner, center air lance, ports on the furnace sidewalls, and air register bias. Methods involving fuel staging will then be discussed. These include fuel injectors aimed radially outward, low velocity injection, fuel injectors located around the burner, and diversion of fuel to the CO-gas. Use of fuel/air injectors downstream in the furnace was not tested.

The injectors out-of-service (O.O.S.) method of staging is essentially an intra-burner version of the burners-out-of-service (B.O.O.S.) technique that has been highly effective in reducing NO_x in large multi-burner utility

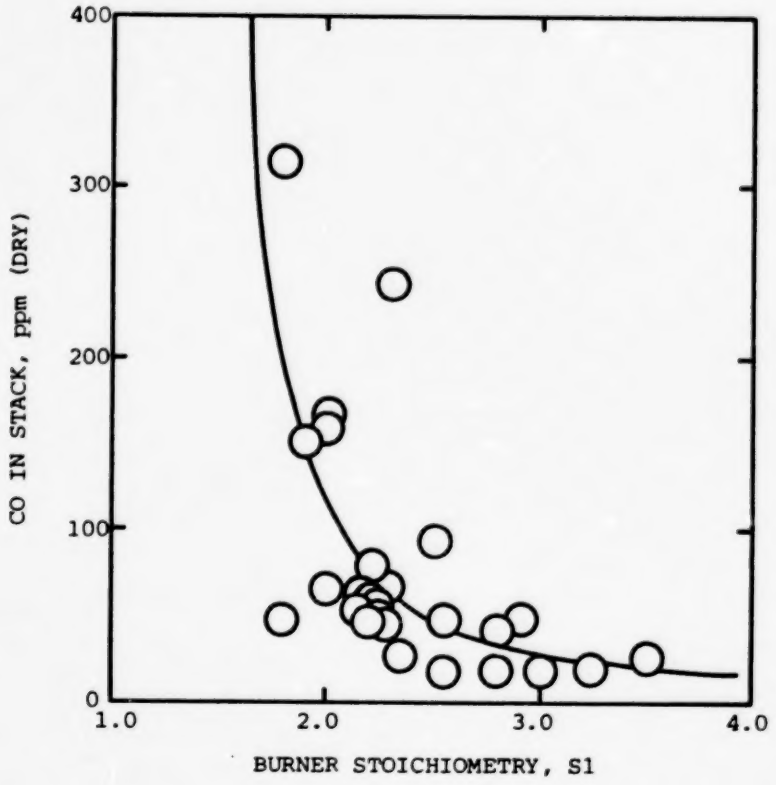

Figure 9. CO Versus Burner Stoichiometry - Unstaged

boilers. Fuel was discontinued to selected injectors (see Figure 2) with the same total fuel entering the furnace via the in-service injectors. This created a more fuel-rich combustion zone at the burner and thus was a method of staging. Various injector patterns were tested to locate the best set of injectors through which to inject the fuel. Overall, the pattern tests indicated that the optimum location for injectors O.O.S. is on the burner quadrant farthest removed from the CO-gas entry. Sheltering the CO-gas from immediate mixing with the combustion air by the uneven distribution of the gas fuel provided a reduction in NO_x.

The laboratory furnace included eight air ports (NO_x ports) in the burner wall arranged in a circle around the burner. Each port was equipped with a conical plug for opening and closing it. When open, the ports admitted air to the furnace directly from the windbox and reduced the amount of air entering via the burner. Similarly to injectors O.O.S. testing, the NO_x ports were pattern-tested to locate the best NO_x port-open pattern. The results of these tests were similar to the injectors O.O.S. results in that opening the ports farthest removed from the CO-gas entry gave the best NO_x reduction. CO control was good; all patterns produced 138 ppm or less CO.

Center air staging employed an air lance on the burner centerline which was supplied by a separate blower. This consisted of a 3.175 cm O.D. tube with 0.071 cm wall thickness. The depth of immersion of the lance was varied from 39 to 70 cm from the end of the burner throat. Air exited the lance straight ahead, with no radial or swirl velocity component.

Torus air staging employed a torus (donut)-shaped air manifold located 1.68 m from the burner (see Figure 3). The torus injected air radially inward toward the furnace centerline via 32 orifices of 1.43 cm diameter.

Figures 10 through 13 compare NO_x and CO characteristics of each staging method to those of unstaged operation (from Figures 5, 8, and 9). It is important to point out that the data presented in these figures are based on assumptions made in calculating burner stoichiometry. As such, the accuracy of calculated burner stoichiometry values may not be the same for all the staging methods tested. A low level of accuracy for calculating the burner stoichiometry is suspected for the injectors O.O.S. and NO_x port methods since more extensive assumptions were made in performing these calculations. A higher level of confidence exists for data developed using the torus and center lance assemblies since for these methods the staging air was measured rather than calculated.

The injectors O.O.S. method (Figure 10) produced higher NO_x levels than unstaged combustion at stoichiometries below approximately 1.8 but also produced substantially lower CO levels, enabling operation at lower stoichiometries. The NO_x port-open results (Figure 11) indicate higher NO_x than unstaged operation at stoichiometries below approximately 2.0 for symmetrical air and 1.7 for bottom air. In considering these results for the injectors O.O.S. and NO_x port methods of staging, it should be recalled that calculation of burner stoichiometry for both of these methods is only approximate. Comparisons of NO_x and CO levels at specific stoichiometries to those produced

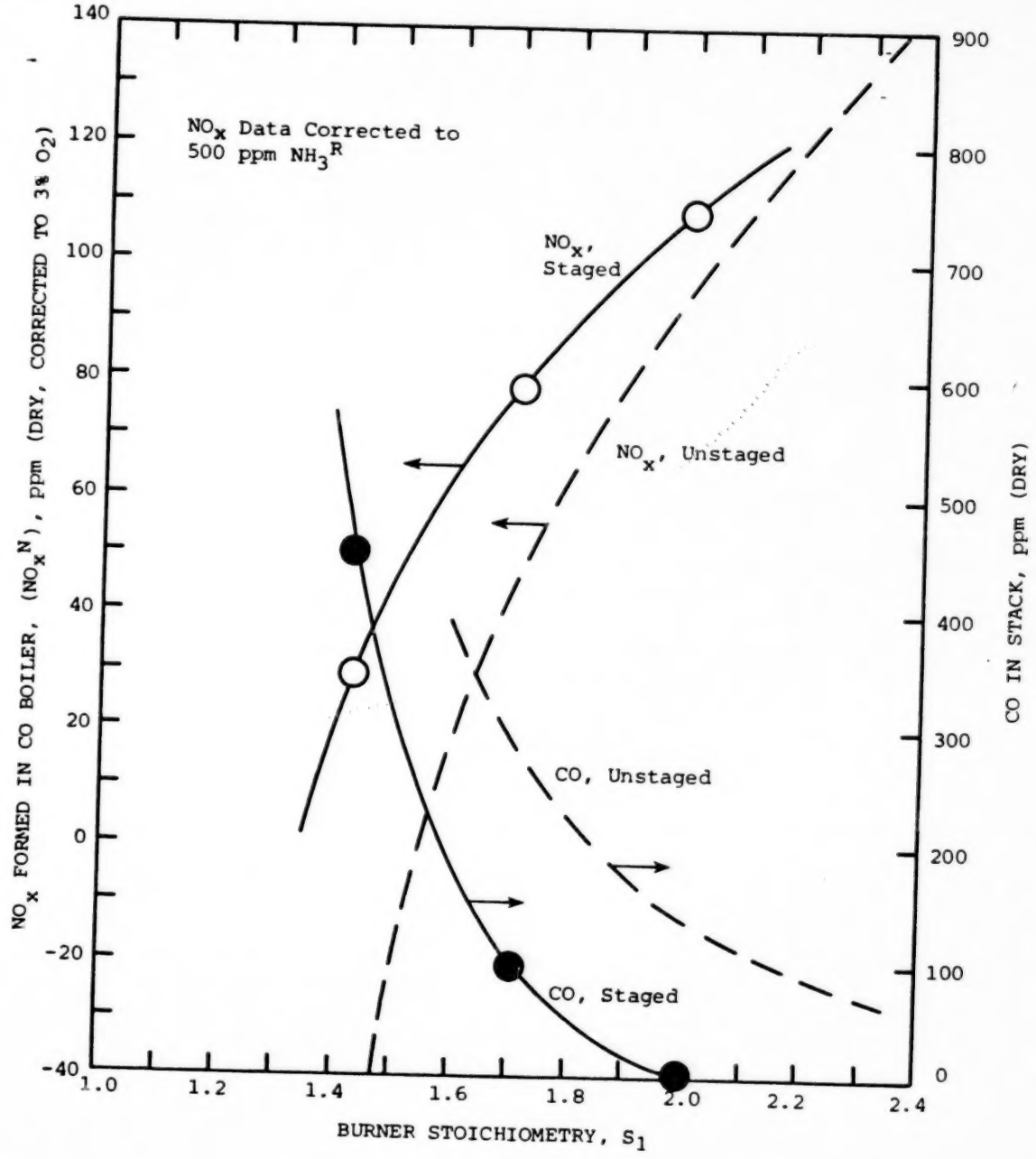

Figure 10. NO_x and CO Versus Burner Stoichiometry with Staged Combustion--Injectors Out-of-Service

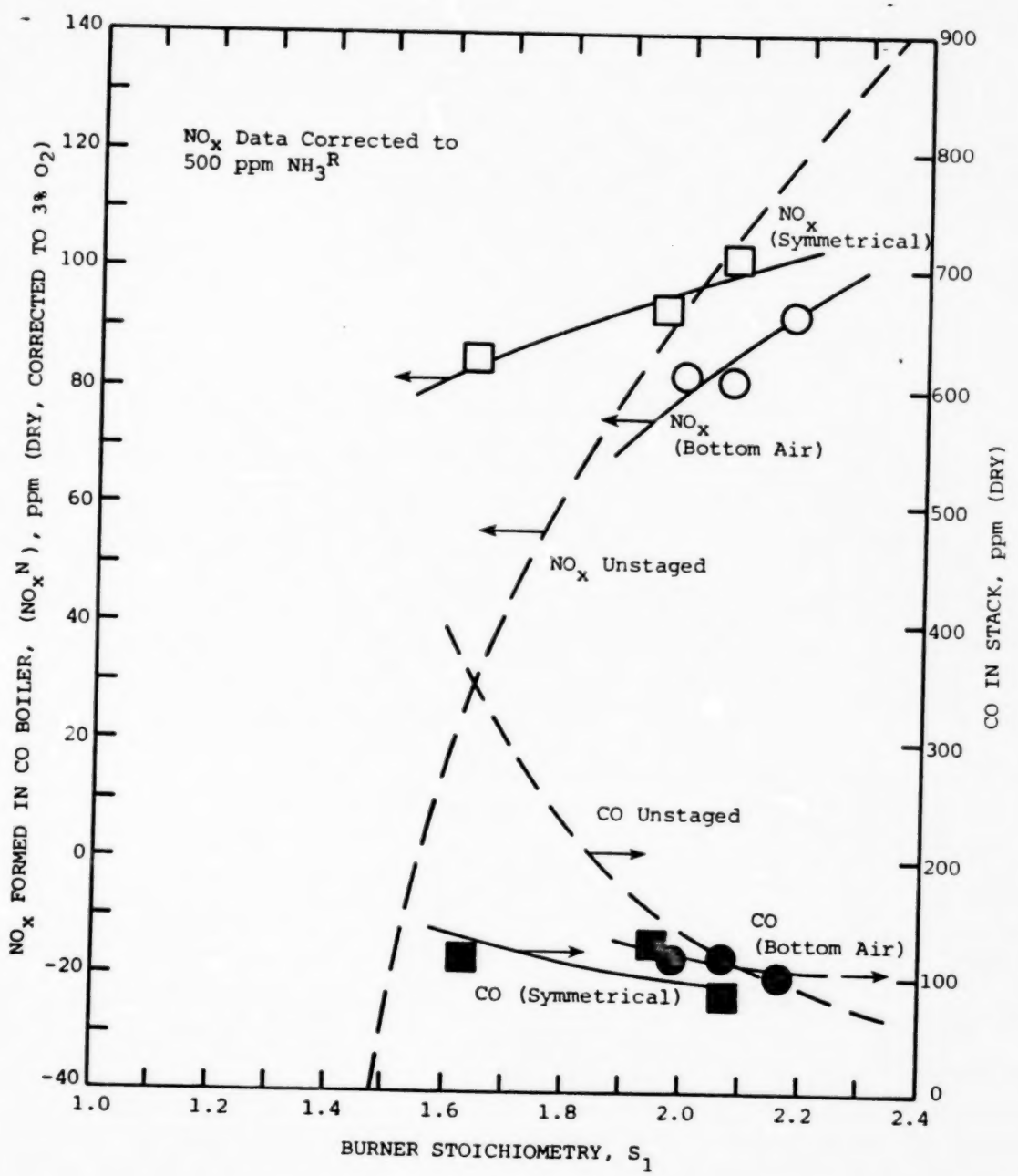

Figure 11. NO_x and CO Versus Burner Stoichiometry with Staged Combustion--NO_x Ports Open

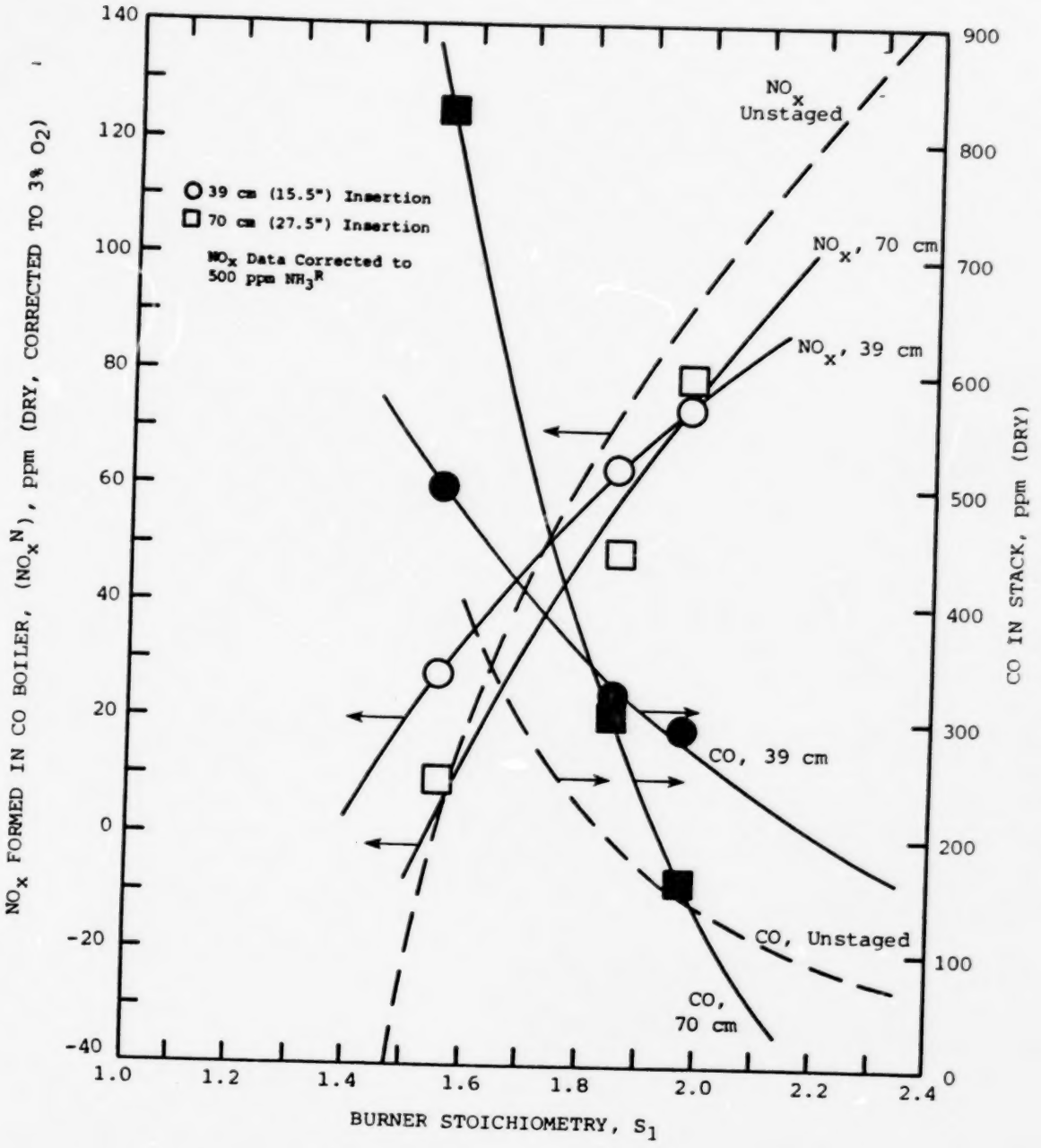

Figure 12. NO_x and CO Versus Burner Stoichiometry with Staged Combustion--Center Lance Air

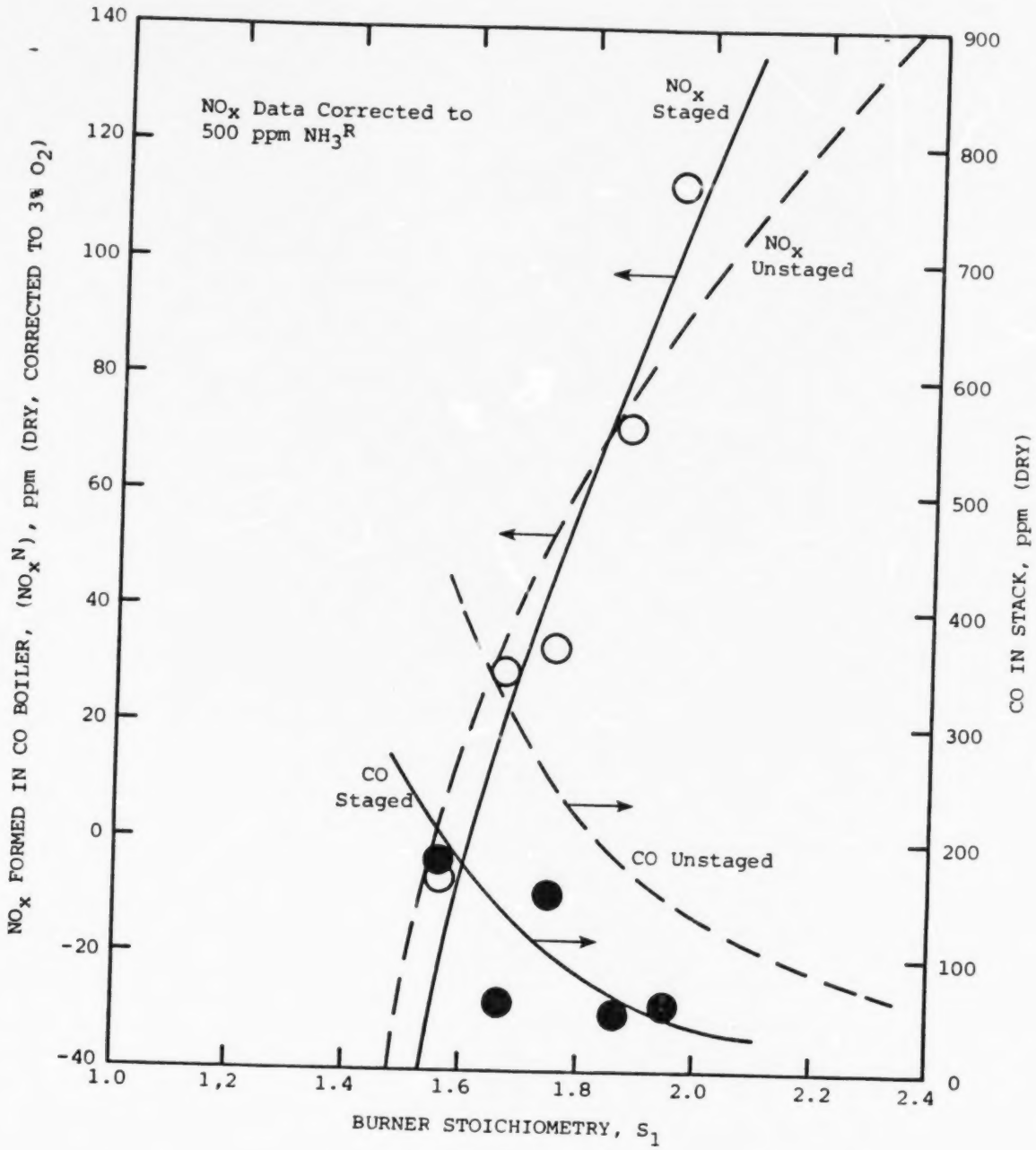

Figure 13. NO_x and CO Versus Burner Stoichiometry with Staged Combustion--Torus Air

by the unstaged burner may be less meaningful than comparisons of the NO_x-versus-CO characteristics of the various configurations, as discussed below.

Use of center air (Figure 12) resulted in very poor CO control, much worse than unstaged operation. Furthermore, NO_x levels were higher than unstaged NO_x levels at stoichiometries below approximately 1.7. The poor CO control probably resulted from the center air's being injected straight ahead. The swirl pattern in the furnace was apparently not strong enough to induce sufficient radial progress of the center air to allow it to mix fully with the CO-gas.

Torus air (Figure 13) resulted in NO_x levels comparable to the unstaged burner and better CO control over the full range of stoichiometry tested. This was made possible by location of the air at the outer periphery of the furnace where unoxidized CO-gas would tend to be located, plus design of the torus for optimum mixing of the staged air with the CO-gas.

Figure 14 compares the NO_x-versus-CO tradeoffs for the various staging methods tested. Use of torus air gave by far the best results, achieving much lower NO_x formation at comparable CO levels than unstaged combustion or any of the other staging methods. As indicated in the figure, the data indicate that using torus air, the laboratory boiler can be operated with zero net NO_x formation at a CO level of approximately 170 ppm. Very limited data on operation with bottom NO_x ports open indicated that this technique also may have very good NO_x-versus-CO characteristics. NO_x port air would not, however, appear to be as effective as torus air.

A final method of air staging that was tested was that of air register bias. The burner air register consisted of 16 vanes in a circle around the throat inlet. These vanes could be adjusted individually from 0° (wide open) to 90° (closed). Their normal position was 45°. In the first series of tests, air vanes were opened simultaneously to reduce air swirl. This produced a minor NO_x reduction but was limited by flame instability. In a second series of tests, vanes were fully opened on selected segments of the register in order to bias the air and produce some staging of the combustion. This method produced significant NO_x reductions to as low as 87 ppm (net) from a baseline level of 134 ppm. For all tests in the series, except the tests producing an unstable flame, CO levels were well controlled and less than 200 ppm.

The first fuel staging method tested was that of aiming the fuel away from the burner centerline. The fuel injectors were "chisel tip" spuds with a single orifice on one face of the chisel tip. Normal orientation of the orifice was radially inward, toward the burner centerline. In order to stabilize the flame with the injectors in the radial-outward orientation, it was necessary to open the air registers basically to 15°, with vanes 1, 5, 9, and 13 at 35° (1 = top, counting clockwise from outside the furnace). As indicated in Table III, rotation of the fuel injection angle away from the normal radial-inward position to a radial-outward position had a strong effect on the NO_x level. Creating a fuel-rich outer zone in the flame for NH_3 destruction apparently was successful. However, as also noted in Table III, a

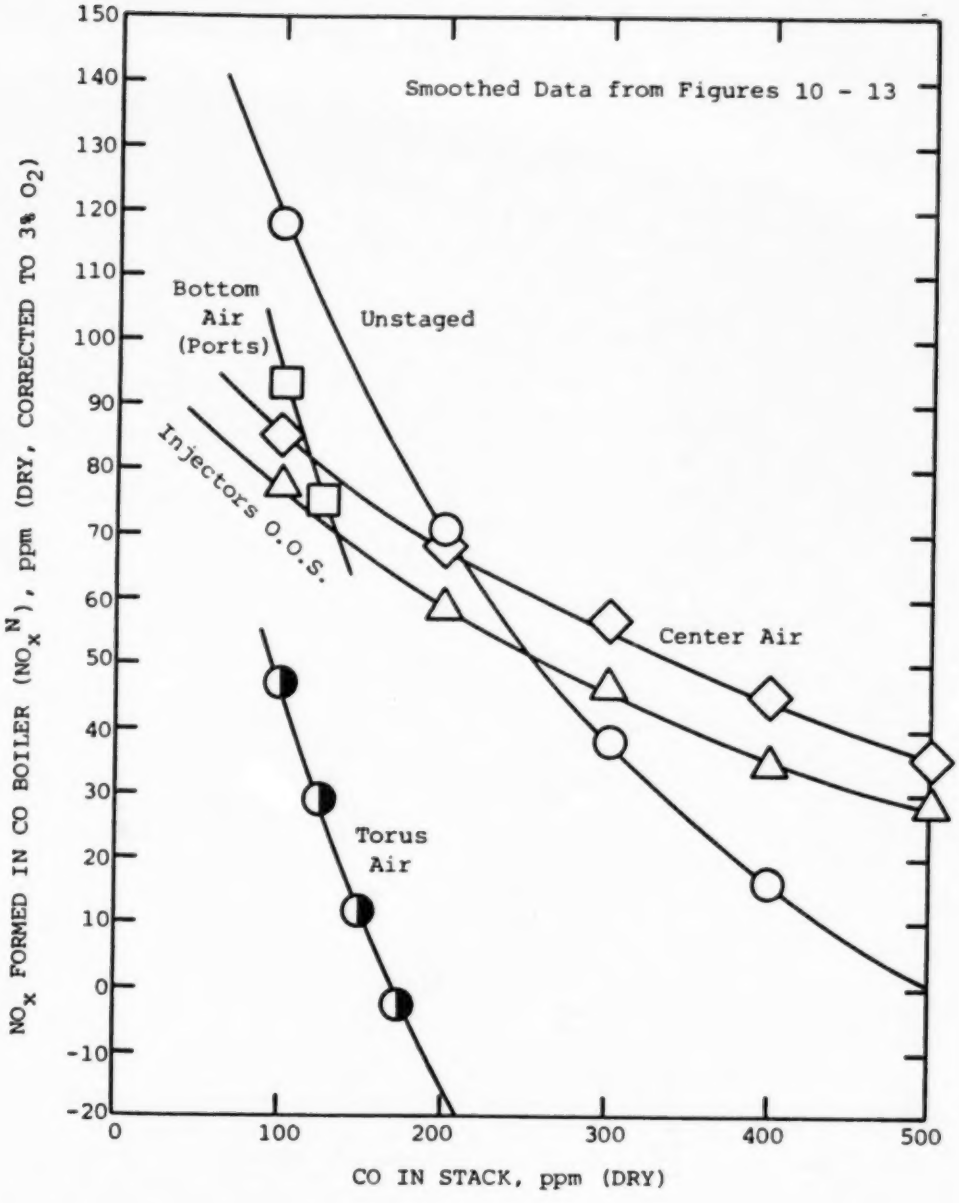

Figure 14. NO_x Versus CO for Various Methods of Staging the Combustion

Table III. Effect of injectors radially outward on NO_x formation.

Injector Orientation	Vane Settings	NO_x^N, ppm (dry, corr. to 3% O_2)[a]	CO, ppm (dry)
Radially In	All 45°	136	50
Radially Out	All 15° Except 1, 5, 9, 13-35°	23	470

[a]Corrected to 500 ppm NH_3^R.

high CO level also resulted with the injectors in the radial-outward position. It is probable that an optimum injection angle could be achieved by an intermediate degree of injector rotation which would produce an acceptable CO level while still retaining much of the NO_x reduction effect.

In order to test the effect of lower fuel injection velocity, low-velocity injectors were substituted for the normal injectors. The low-velocity injectors differed from the normal injectors only in having larger injector orifices (0.4763 cm vs. 0.3175 cm diameter). The objective was to achieve some combustion staging via less optimum fuel/air mixing. The low-velocity injectors increased the NO_x formation. Among the causes suspected for the increase is that reducing the injection velocity of the gas altered the gas flame geometry. The delayed gas mixing caused more of the fuel to burn on the outer surface of the combustion air stream in the form of a diffusion flame. This is suspected to have caused the flame to expand closer to the furnace wall where CO-gas is present, promoting NH_3 conversion to NO_x.

The two remaining fuel-staging approaches that were tested -- relocation of fuel to injectors surrounding the burner or diverting fuel to the CO-gas -- were both found to increase the NO_x.

Selection of Best NO_x Reduction Approaches

Staging combustion using torus air was clearly the best NO_x reduction approach tested in the laboratory. This method produced substantial NO_x reductions without sacrificing CO control. Air staging using a center air lance on the burner axis was not as successful due to a tendency to produce high CO levels. Staged air admitted via ports located around the burner also appeared promising, especially using ports located below the burner; however, this method did not show potential to be as effective as torus air.

In the field, torus air translates to injection of staged combustion air well downstream of the burner transverse to the overall furnace flow. This could be accomplished by a torus, as was done in the laboratory, or by ports in the furnace enclosure. Side ports alone may or may not be sufficient. It is possible that top and bottom ports would be required as well. Center air could be used as an adjunct to torus air, particularly for a furnace having low length-to-diameter ratio.

Asymmetric air register settings to bias the air works reasonably well (single-burner furnace was tested) but would be difficult to effect on a consistent basis in the field. The best adjustment may vary with boiler load, which would be difficult to accomplish.

Injectors O.O.S. significantly reduced NO_x; however, this method leads to high CO. NO_x-versus-CO characteristics would have to be verified over a load range on any particular unit. This method may be of value where modest NO_x reduction is required.

Modification of fuel gas injection angle and velocity showed a strong capability to reduce NO_x. Although optimum conditions were not reached, this method probably deserves more exploration.

Conclusions

Presented below are the major conclusions drawn from the results of the laboratory testing. In reviewing these conclusions it should be borne in mind that the tests were performed on a single-burner horizontal furnace with CO gas admitted via a concentric annulus surrounding the burner throat. All tests were on natural gas fuel. The ratio of CO-gas to total stack gas was approximately 0.65 (dry basis). The CO-gas contained approximately 2 percent CO, 500 ppm NH_3, and 120 ppm NO_x. Some of the conclusions may be very specific to some of these test conditions and others may be more general.

1. All the test program objectives were achieved: the laboratory model was shown to accurately reproduce the emission characteristics of a full-scale CO boiler, the effect of operating variables was determined, and several promising combustion modifications for NO_x reduction were identified.

2. NO_x formed in the CO boiler is due mainly to conversion of NH_3 entering with the CO-gas.

3. The most important variables influencing the NO_x level are the NH_3 content of the CO-gas and the burner stoichiometry (air/fuel ratio).

4. Air staging was found to be the best NO_x control method. Addition of staged air well downstream of the burner with good cross-mixing produces the best results.

Applicability to Full-Scale Boilers

The research program has shown that:

- Key operational variables influencing NO_x formation in refinery CO boilers are the NH_3 level in the CO-gas and the burner stoichiometry.

- The most effective NO_x control method is to stage the combustion using second-stage air admission downstream in the furnace similar to the torus air used in the laboratory.

To the degree that the NH_3 level in the CO-gas can be reduced -- possibly by selecting lower-nitrogen crudes or by adjustment of catalytic cracking unit operating parameters (if possible) -- this will reduce NO_x formation in the CO boiler. This approach, however, will probably not be practical in most cases. Control of burner stoichiometry (low excess air) is probably practiced to the extent possible on most CO boilers but is limited by

the need to run sufficient excess air to burn out all CO contained in the regenerator gas.

- Staging combustion provides the added flexibility needed to control burner stoichiometry while meeting the objective of good CO oxidation. Use of a staged air torus located downstream in the furnace, as practiced in the laboratory, could be adapted to full-scale boilers or could be translated into staged air ports located in the furnace walls. Previous efforts to stage refinery CO boilers, as carried out by equipment manufacturers, have not been based on accurate knowledge of the correct design parameters and hence have not generally produced the desired results. The laboratory program has demonstrated that, when properly designed, combustion air staging is an effective NO_x reduction technique for refinery CO boilers.

Acknowledgment

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